Optical multiple pulse sequences for multiphoton selective excitation and enhancement of forbidden transitions

W. S. Warren and Ahmed H. Zewail

Citation: The Journal of Chemical Physics **78**, 3583 (1983); doi: 10.1063/1.445186
View online: http://dx.doi.org/10.1063/1.445186
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/78/6?ver=pdfcov
Published by the AIP Publishing

Optical multiple pulse sequences for multiphoton selective excitation and enhancement of forbidden transitions

W. S. Warren[a)]

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Ahmed H. Zewail[b)]

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 1 September 1982; accepted 9 September 1982)

In this paper we present novel and simple pulse sequences for enhancing the intensity of forbidden or highly nonresonant optical transitions. These sequences provide a straightforward approach to circumventing the most serious limitation of optical coherent transient spectroscopy: Available laser intensities are often insufficient to excite a significant fraction of the ground state population into desired excited states, either because of large inhomogeneous broadening or, in the case of multiphoton absorption, large anharmonicities. Optical phase modulation (which can be produced by an acousto-optic modulator) or amplitude modulation (which can be produced by an interferometer) with carefully chosen pulse flip angles and delays can effectively remove even very large energy mismatches, thus permitting essentially complete population inversions arbitrarily far from resonance. Coherent averaging theory and computer calculations are used to derive particularly valuable sequences. Pumping enhancement of 10^3–10^5 (depending on individual molecular parameters) for these modulated pulse sequences are predicted. Specific applications to multiphoton pumping of local vibrational modes are discussed.

I. INTRODUCTION

In a recent communication and papers we showed that optical pulse trains (or sequences) with specified phases can be used to suppress incoherent background signals, enhance coherent signals, narrow optical lines, and separate different relaxation channels in multilevel systems.[1,2] The method for generating these sequences relies on an extension of the technique of Orlowski and Zewail[3] which utilizes acousto-optic (AO) modulation of a single-mode laser. The AO modulator acts as a mixer and, hence, the phase of the optical wave can be precisely controlled by controlling the phases of the rf which forms the sound-wave "grating" on the AO modulator. With these phase controls one can therefore perform the optical analog of NMR multiple pulse spectroscopy. In Refs. 1 and 2, we demonstrated the optical analog of NMR composite pulse sequences, and the use of different sequences (such as XXX–$XX\bar{X}$) to eliminate background spontaneous emission in iodine gas at low pressures. Here, we present novel and simple sequences for enhancing the intensity of forbidden or highly nonresonant transitions in the optical region.

The problem we will address is a very common one: the available laser intensity is insufficient to excite a significant fraction of the ground state population into the desired excited states, either because of large inhomogeneous broadening or a large spread of vibronic transition frequencies. In either case energy mismatches which cannot be overcome by a single laser pulse can be effectively eliminated by multiple pulse trains. Applications to overtone and two-photon spectroscopy are given, and the possibility of essentially complete population inversion into nonresonant levels is demonstrated.

II. POPULATION ENHANCEMENT IN TWO-LEVEL SYSTEMS THROUGH COMPOSITE PULSE TRAINS

A. Preliminaries for single pulse excitation

The effects of an intense coherent pulse on a closed two-level system are thoroughly documented[4–9] and will be only briefly summarized here. In NMR,[6] microwave,[7] or optical spectroscopy[8,9] the semiclassical interaction between radiation and matter ($\mu\cdot\mathbf{B}$ or $\mu\cdot\epsilon$) gives

$$\mathcal{H}_{\rm int}=\hbar\omega_{1x}\cos(\omega t+\phi)\sigma_x\,, \tag{1}$$

where the radiation field is assumed to be directed along the x axis and $\omega=\mu_x|\mathbf{B}|$ (in NMR) or $\mu_x|\epsilon|$ (in microwave or optics). σ_x is one of the Pauli matrices of the two-level system. The phase $\phi(t)$ will include a directional dependence $\mathbf{k}\cdot\mathbf{r}$ in the optical case, but longer wavelengths normally make this term unimportant at rf or microwave frequencies.

There will also be a diagonal term in the Hamiltonian reflecting the energy difference $\hbar\omega_0$ between ground and excited states:

$$\mathcal{H}_{\rm diag}=\begin{pmatrix}+\frac{1}{2}\hbar\omega_0 & 0\\ 0 & -\frac{1}{2}\hbar\omega_0\end{pmatrix}=\hbar\omega_0\sigma_z\,, \tag{2}$$

where the energy difference arises from interactions with an applied static field in NMR, from angular momentum changes in microwave spectroscopy, and from different vibronic wave functions in optical spectroscopy.

If ω_0 is sufficiently near to ω to make only single photon absorption important (i.e., 2ω is far from reso-

---

[a)] National Science Foundation Postdoctoral Fellow at Caltech, 1981.

[b)] Alfred P. Sloan Fellow and Camille and Henry Dreyfus Foundation Teacher–Scholar.

 0021-9606/83/063583-10$2.10

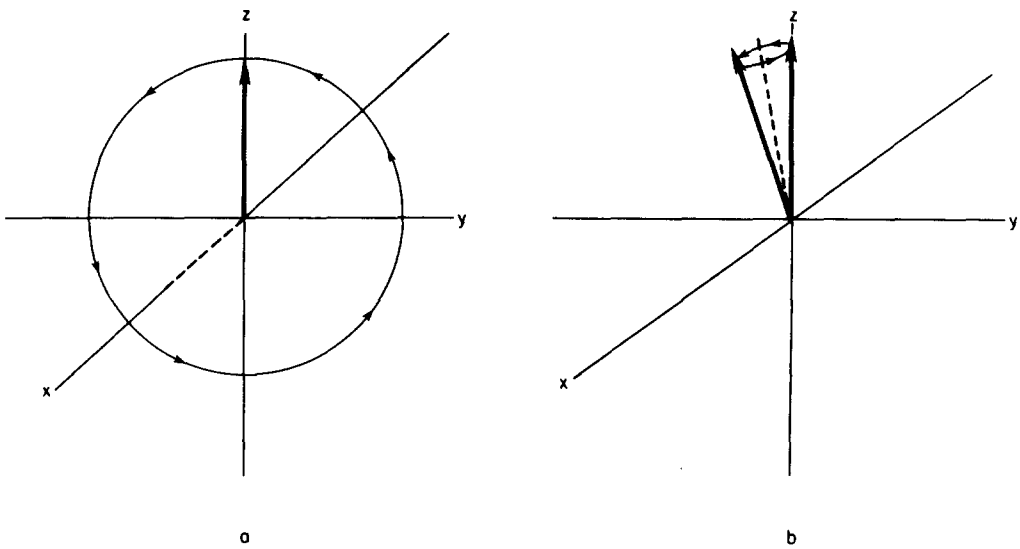

FIG. 1. Population inversions generated by applied laser pulses as a function of resonance offset. Part (a) corresponds to irradiation directly on resonance. Such irradiation can take the initial population distribution (represented here by a pseudo-polarization vector along the z axis (Ref. 5)] into a complete population inversion with a so-called π pulse. If the resonance offset $\Delta\omega$ is much larger than the pulse bandwidth (Rabi frequency) ω_1, as in part (b), then a single pulse can only slightly perturb the system, generating a maximum excited state population of $\omega_1^2/(\Delta\omega^2+\omega_1^2)$. Normally the inhomogeneous broadening of optical transition is so large that most molecules are always far from resonance, so that relatively few excited molecules can be produced.

nance), then the density matrix time evolution of the system under the combined Hamiltonian $\mathcal{H}_{\rm int}+\mathcal{H}_{\rm diag}$ can be written in the rotating wave approximation[10] as

$$\tilde{\rho}(t)=\exp(-i\tilde{\mathcal{H}}t/\hbar)\tilde{\rho}(0)\exp(+i\tilde{\mathcal{H}}t/\hbar)\,, \tag{3}$$

$$\tilde{\mathcal{H}}=\hbar(\Delta\omega\sigma_z+\omega_1\cos\phi\sigma_x+\omega_1\sin\phi\sigma_y)\,, \tag{4}$$

$$\Delta\omega=\omega-\omega_0\,. \tag{5}$$

The tildes have been introduced in $\tilde{\mathcal{H}}$ and $\tilde{\rho}$ to conform with the conventional notation for rotating frame operators. However, for simplicity of notation they will henceforth be omitted, although the rotating frame will still be assumed. Equation (3) is valid over any interval in which ω_1 and ϕ are constant and relaxation terms can be neglected. The equilibrium density matrix will generally be

$$\rho_{\rm eq}=C\begin{pmatrix}\exp(-\hbar\omega_0/2kT) & 0\\ 0 & \exp(+\hbar\omega_0/2kT)\end{pmatrix}, \tag{6}$$

where the proportionality constant C makes $\mathrm{Tr}(\rho_{\rm eq})=1$. This can always be written as

$$\rho_{\rm eq}=1+\beta\sigma_z\,, \tag{7}$$

where usually $\beta\ll 1$ in NMR or microwave (the high temperature limit) and $\beta\sim 1$ in optical spectroscopy (the low temperature limit). In either case the identity matrix is unimportant in the time evolution, since it commutes with $\mathcal{H}$. Thus, only the σ_z term contributes to the dynamics.

To calculate the effects of a single pulse, assume $\phi=0$. The Hamiltonian in Eq. (4) then rotates the σ_z component of the initial density matrix around an axis defined by $\Delta\omega\sigma_z+\omega_1\sigma_x$. If $\Delta\omega=0$ (exact resonance) the initial condition is completely reversed when $\omega_1 t=\pi$, corresponding to the maximum possible population inversion [Fig. 1(a)]. In optical spectrscopy this puts every molecule in the excted state, but in NMR or microwave the inversion will be less, with the β term in $\rho_{\rm eq}$ of Eq. (7) changing sign. Other values of ϕ correspond to merely phase shifting the radiation field; the net effect is identical to $\phi=0$, except that any induced coherences are also shifted.

If $\Delta\omega\neq 0$ complete inversion from a single pulse is not possible. The rotations now are restricted to a cone [Fig. 1(b)]. The maximum inversion is created by a pulse of width $t_p=\pi/(\Delta\omega^2+\omega_1^2)^{1/2}$ which takes the σ_z coefficient from β to $\beta[(\Delta\omega)^2-\omega_1^2]/[(\Delta\omega)^2+\omega_1^2]$. This reduced effect is a particularly serious limitation in optical spectroscopy, where typical inhomogeneous linewidths ($\sim$0.2–30 GHz) give a spread to $\Delta\omega$ which is at best comparable to, and usually much greater than, accessible values of ω_1. Then single pulse irradiation can only significantly affect a small fraction of the line shape.

B. Composite pulse trains and large population inversion

It has been known for many years in NMR that several pulses back-to-back, with phase shifts between them, can be less sensitive to inhomogeneities than is a single pulse.[11] We have shown recently that these composite pulses are also useful in optical spectroscopy, and have demonstrated significant signal enhancements for fluorescence and echo measurements.[12] In essence, the phase shift changes the rotation cone of Fig. 1(b) so that other regions of this three dimensional operator space are accessible.

One application of particular interest in optical spectroscopy is the use of composite pulse trains to create large population inversions even when $\Delta\omega\gg\omega_1$. Consider, for example, the effects of a single pulse with

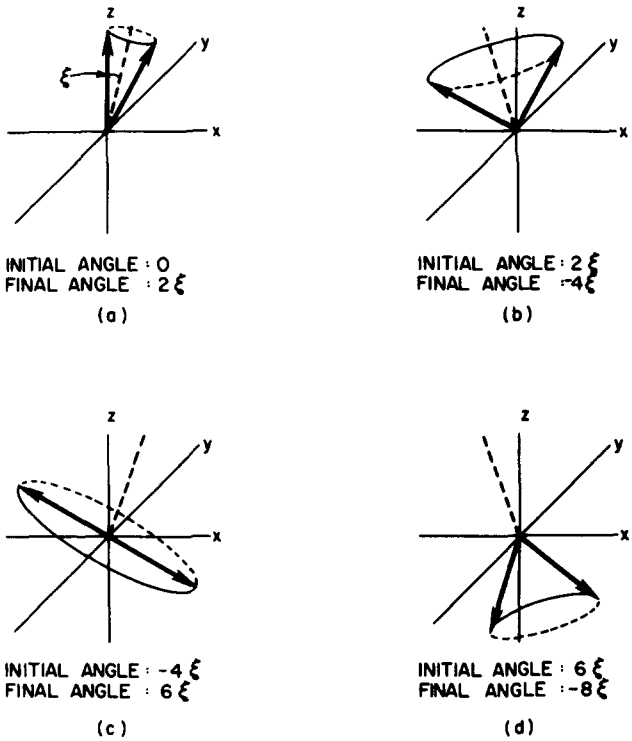

FIG. 2. Phase modulated pulse sequences can create essentially complete population inversions for arbitrarily large resonance offsets, within the limits of validity of the rotating wave approximation (see the text). In part (a) a single pulse of length $t_p = \pi(\Delta\omega^2 + \omega_1^2)^{-1/2}$ moves the pseudopolarization to a position 2ξ from the z axis, where $\xi = \tan^{-1}(\omega_1/\Delta\omega)$. This pulse is followed in part (b) by a pulse of the same length, but 180° out of phase with the first. The phase shift can be readily produced by acousto-optic or electro-optic modulation. This changes the rotation axis from $+\xi$ to $-\xi$, so that after the pulse the pseudopolarization is -4ξ from its initial position. Further repetitions of this two-pulse sequence, which would be termed $(\bar{X} - \bar{X})$ in standard NMR notation, give a large inversion [parts (c) and (d); more repetitions would be needed for larger $\Delta\omega/\omega_1$]. Since each individual pulse is very short the sequence is very efficient (see the text).

$\phi = 0$ in Eq. (4) (in the standard NMR notation this is called an x pulse), followed immediately by a pulse with $\phi = \pi$ (an $\bar{x}$ pulse). To create a large effect at some specific value of $\Delta\omega$, choose the width t_p of each pulse such that

$$(\Delta\omega^2 + \omega_1^2)^{1/2} t_p = \pi \ . \tag{8}$$

The rotation axis of the first pulse makes an angle $\xi = \tan^{-1}(\omega_1/\Delta\omega)$ with the z axis, and the π rotation takes σ_z to a position 2ξ away from the initial state [Fig. 2(a)]. The $\bar{x}$ pulse, which gives a rotation axis of $-\xi$ with respect to σ_z, takes the reduced density matrix to -4ξ [Fig. 2(b)]. This process can be repeated, as in Figs. 2(c) and 2(d). In fact, the sequence $(x - \bar{x})_N$ will give a final reduced density matrix which is $(-1)^N 4N\xi$ away from the equilibrium state, so that if N is large enough virtually complete inversion can be produced for arbitrarily large $\Delta\omega/\omega_1$ (subject to the validity of the rotating wave approximation, which requires the fractional resonance mismatch $\Delta\omega/\omega_0$ to remain small.)

The role of the phase shift can also be seen mathematically by multiplying together the propagators for the two pulses:

$$U_x = \exp[-i(\Delta\omega\sigma_z + \omega\ \sigma_x)t] = \begin{pmatrix} -i\cos\xi & -i\sin\xi \\ -i\sin\xi & i\cos\xi \end{pmatrix} , \tag{9}$$

$$U_{\bar{x}} = \exp[-i(\Delta\omega\sigma_z - \omega_1\sigma_x)t] = \begin{pmatrix} -i\cos\xi & i\sin\xi \\ i\sin\xi & i\cos\xi \end{pmatrix} , \tag{10}$$

$$U_x U_{\bar{x}} = \begin{pmatrix} -\cos 2\xi & -\sin 2\xi \\ -\sin 2\xi & -\cos 2\xi \end{pmatrix} = -\exp(i4\xi\sigma_y) \ . \tag{11}$$

The relation $[(\Delta\omega)^2 + \omega_1^2]^{1/2} = \pi$ was used to simplify Eqs. (9) and (10); the general expression for the two-level propagator with arbitrary $\Delta\omega$, ω_1, and t can be found in many other references, among them Ref. 2. The product of the two propagators is, apart from a physically irrelevant sign, identical to the rotation which would be produced by a single pulse on resonance with flip angle 4ξ. The total pulse sequence duration $T = 2t_p = 2\pi(\Delta\omega^2 + \omega_1^2)^{1/2}$, which implies

$$\omega_1 T \sim 2\pi\xi \qquad (\Delta\omega \gg \omega_1) \tag{12}$$

so the excitation (far from resonance) is $4/2\pi \sim 63\%$ as efficient in producing excited state population at $\Delta\omega$ as it would be if the resonance offset were completely absent.

The two pulses can be repeated as many times as needed to give a good $\pi/2$ pulse (maximizing σ_x or σ_y) or π pulse (maximizing the inversion). Thus, the composite sequence can be used as a building block for such multiple pulse sequences as photon echoes which are optimized by $\pi/2$ or π pulses and which would normally be totally useless this far from resonance.

The arguments presented above work equally well if $\Delta\omega$ is replaced by $-\Delta\omega$. In addition, this sequence will produce large excited state populations at resonance frequencies of $\pm 3\Delta\omega$, $\pm 5\Delta\omega$, ..., $N\Delta\omega$, where N is any odd integer. At $N\Delta\omega$ a pulse of length t_p gives a rotation of $\sim N\pi$ [see Eq. (8)], so the only change in Fig. 2 is that ξ (and hence the total flip angle) is reduced by a factor of N. This effect can be made intuitively obvious by noting that the phase shifts provide a square wave modulation with period $T = 2\ t_p \sim 2\pi/\Delta\omega$ [see Eq. (8)]. This produces sidebands at $\pm N\ \Delta\omega$ with the same relative intensities as the flip angle ratios derived above.

Phase modulation at frequency $\Delta\omega/2\pi$ could be conveniently produced by feeding a continuous single-mode laser into an acousto-optic modulator with a sufficiently short rise time. But this raises an interesting technical question. The rise time of the output laser pulse will certainly not be less than the rise time of the acoustic wave, and in practice it is substantially longer than this minimum.[13] The rise time of the acoustic wave gives the frequency bandwidth of the modulator. Thus if phase modulation at $\Delta\omega/2\pi$ is possible, it must also be possible to raise the rf frequency by $\Delta\omega/2\pi$, and thus hit the transition on resonance. Therefore, while this sequence does provide a method of shifting the effective resonance frequency of the laser, equally large shifts can be accomplished by simpler means.

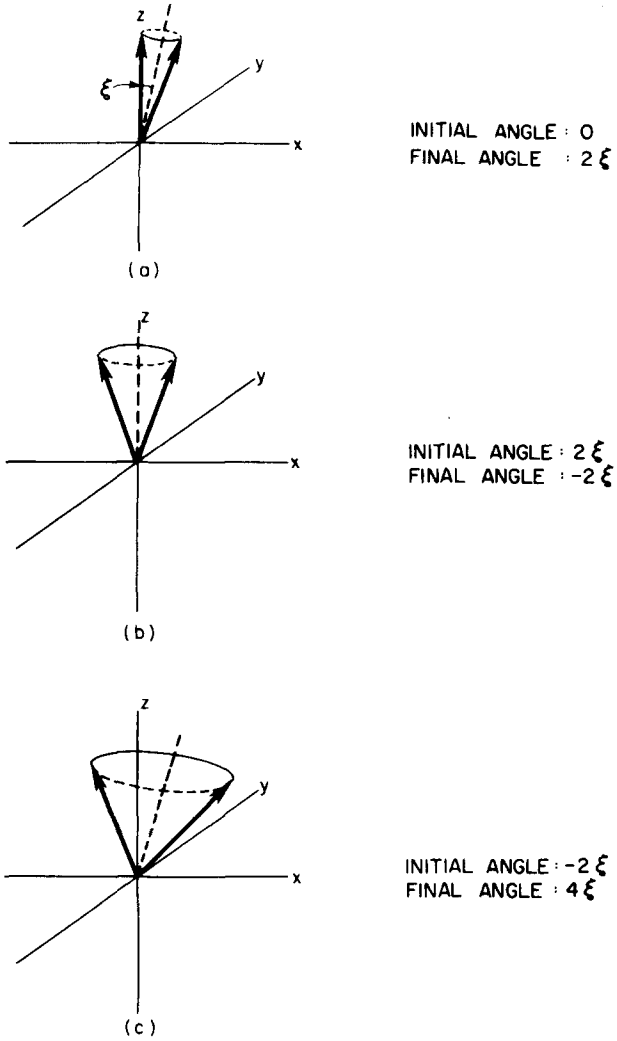

FIG. 3. Large inversions can also be produced by putting delays between the pulses of $t_d = \pi/\Delta\omega$ and omitting the phase shifts. Part (a) is identical to Fig. 2(a). The delay in part (b) rotates the pseudopolarization away from its position after the first pulse. Now a second pulse with the same phase (rotation axis) as the first [part (c)] generates an increased inversion. This amplitude modulation can be readily generated by an interferometer (see the text).

A slight modification on this sequence makes it much more useful. Instead of using phase shifts, insert spaces between the pulses such that the Hamiltonian during the spaces ($\Delta\omega\sigma_z$) rotates the reduced density matrix away from the cone, as in Fig. 3. The first pulse [part (a)] lasts for $t_p = \pi/(\Delta\omega^2 + \omega_1^2)^{1/2}$, as before, but now this pulse is followed by a delay of $t_p = \pi/\Delta\omega$ [part (b)]. A second pulse with the same phase as the first [part (c)] creates an increased inversion. A similar approach has been used in NMR in the so-called DANTE sequence[15] to selectively give a large inversion to one particular group of spins without seriously perturbing others.

This sequence can also be viewed as a square wave modulation of a continuous wave, plus an added dc offset. Thus there are still substantial inversions at all odd multiples of $\Delta\omega$ (Fig. 4). However, this amplitude modulation can be achieved at a much faster rate than phase modulation. For example, a single short pulse fed into a parallel plate interferometer with spacing d produces a pulse train with spacing $t_p + t_d = 2d/c$. The output pulses will be in phase if the interferometer is correctly aligned at the laser frequency, making d an exact multiple of λ. Since pulse flip angle is proportional to the square root of the pulse power, a single pulse with flip angle θ can be approximately divided into N pulses of flip angle $\theta/N^{1/2}$ by the interferometer.[15] If the pulse width and delay are chosen as in Fig. 3, then this train has a substantially increased total flip angle of $\theta(2\sqrt{N}/\pi)$ at $\Delta\omega = \pi/t_d$.[16] Thus, increased flip angles and large resonance frequency changes can be readily achieved by multiple pulse trains.

III. SELECTIVE EXCITATION IN OPTICAL MULTILEVEL SYSTEMS

A. Multiple-quantum selective excitation in nuclear magnetic resonance

The observation of normally forbidden transitions is often useful for spectral simplification, as demonstrated amply in NMR spectroscopy.[17–19] Unfortunately, these transitions are usually only weakly excited by simple pulse sequences.[20] Selective excitation sequences[21–24] use phase shifts to build up one particular set of coherences while cancelling out all others, thus dramatically enhancing the observable signal.

Selective excitation is best understood through the formalism of coherent averaging theory.[25–27] Suppose that the Hamiltonian can be decomposed into a large part ($\mathcal{H}_{big}$) which would generate a readily calculable evolution if no other interactions were present, and a smaller perturbation ($\mathcal{H}_{int}$) which includes everything else. For example, in NMR the rf interaction with matter always is proportional to some linear combination of σ_x, σ_y, and σ_z, so it generates simple rotations and can be used as $\mathcal{H}_{big}$. (The rest of the Hamiltonian may include operators such as $3\sigma_{zi}\sigma_{zj} - \sigma_i \cdot \sigma_j$, and is thus more difficult to analyze.) Suppose further that $\mathcal{H}_{big}$ is cyclic, meaning that after some time t_c the net effect of $\mathcal{H}_{big}$ alone would be zero; again, for example, the sequence might include one x pulse and one $\bar{x}$ pulse, so that the total would have no effect near resonance. In that case $\mathcal{H}_{big}$ can be used to define an interaction representation transforming $\mathcal{H}_{int}$:

$$\tilde{\mathcal{H}}_{int}(t) = U\mathcal{H}_{int}U^{\dagger} , \tag{13}$$

$$U = T\int_0^t \exp(-i\mathcal{H}_{big}t_1)dt_1 , \tag{14}$$

where T is the Dyson time ordering operator.[27] Then the Magnus expansion,[25] which is a perturbation expansion in t_c, permits calculation of the effective propagator $\bar{U}$ for the entire sequence:

$$\bar{U} = \exp(-i\bar{\mathcal{H}}t_c) = \exp[-i(\bar{\mathcal{H}}^{(0)} + \mathcal{H}^{(1)} + \cdots + \bar{\mathcal{H}}^{(n)})t_c] , \tag{15}$$

where:

$$\bar{\mathcal{H}}^{(0)} = \frac{1}{t_c}\int_0^{t_c} \tilde{\mathcal{H}}_{int}(t)\,dt , \tag{16}$$

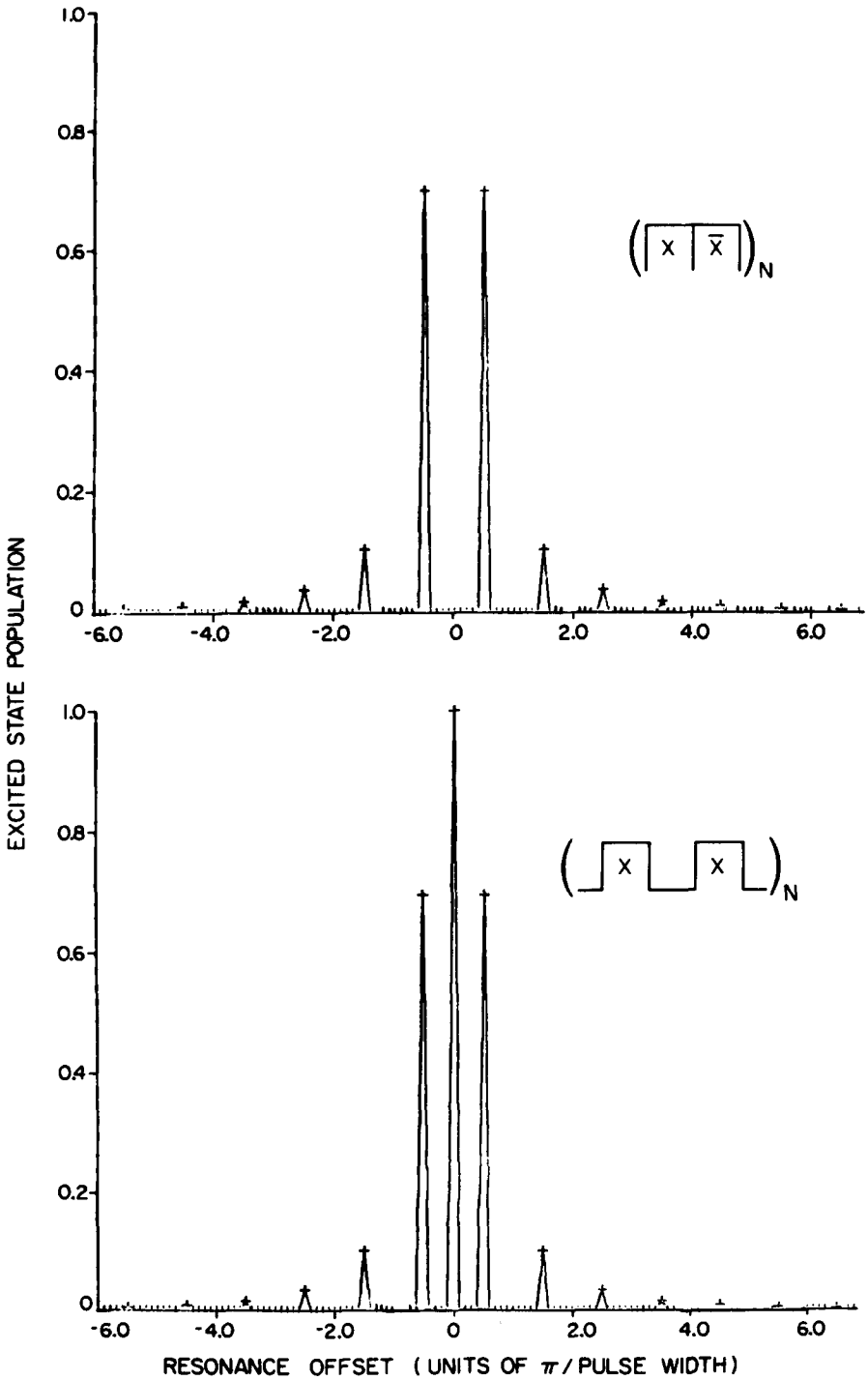

FIG. 4. Comparison of inversions produced by phase or amplitude modulated sequences as a function of resonance offset. In each case the total length of the pulses is set to π/ω_1, so that without any modulation only a central spike of height 1.0 (complete population inversion) would appear. Either sequence provides very large population inversions far from resonance. The effective flip angles correspond to the Fourier components of a square wave for the phase modulated sequence and a square wave plus dc offset for the amplitude modulated sequence. Thus the modulation can be viewed as creating sidebands which overcome the energy mismatch.

$$\bar{\mathcal{H}}^{(1)} = \frac{-i}{2t_c}\int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [\bar{\mathcal{H}}_{\rm int}(t_2), \bar{\mathcal{H}}_{\rm int}(t_1)] \,, \tag{17}$$

$$\bar{\mathcal{H}}^{(2)} = \frac{-1}{6t_c}\int_0^{t_c} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \{[[(\bar{\mathcal{H}}_{\rm int}(t_3), [\bar{\mathcal{H}}_{\rm int}(t_2), \bar{\mathcal{H}}_{\rm int}(t_1)]] + [\bar{\mathcal{H}}_{\rm int}(t_1), [\bar{\mathcal{H}}_{\rm int}(t_2), \bar{\mathcal{H}}_{\rm int}(t_3)]]\} \,. \tag{18}$$

Further details are contained in Ref. 27. $\bar{\mathcal{H}}^{(0)}$ is the zero-order or average Hamiltonian for the sequence; $\bar{\mathcal{H}}$ is called the effective Hamiltonian. The advantage of this approach is that the effects of a complex time dependent process (a pulse sequence) have been approximated by a time independent one.

The basic selective excitation sequence is illustrated schematically in Fig. 5.[21,22] Let $\bar{\mathcal{H}}_0$ represent the effective Hamiltonian of an arbitrary cyclic sequence (duration $\Delta\tau_p$) of pulses and delays. $\bar{\mathcal{H}}_\phi$ represents the same sequence, except that each pulse is phase shifted by an amount $\phi = 2\pi/N$. The propagators $U_0 = \exp(-i\bar{\mathcal{H}}_0\Delta\tau_p)$ and $U_\phi = \exp(-i\bar{\mathcal{H}}_\phi\Delta\tau_p)$ for these two sequences are then related by

$$U_\phi = \exp(-i\phi\sigma_z)\, U_0 \exp(i\phi\sigma_z) \,, \tag{19}$$

$$(U_\phi)_{ij} = (U_0)_{ij} \exp[-i\phi(m_i - m_j)] \,, \tag{20}$$

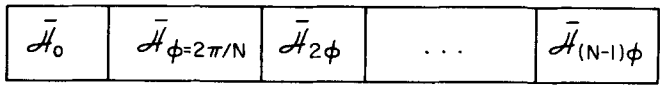

FIG. 5. Schematic illustration of an NMR selective excitation sequence. Here $\bar{\mathcal{H}}_0$ represents the effective Hamiltonian of an arbitrary cyclic sequence of pulses and delays. $\bar{\mathcal{H}}_\phi$ represents the same sequence, except that each pulse is phase shifted by an amount $\phi = 2\pi/N$. These phase shifts are repeated, creating $\bar{\mathcal{H}}_{2\phi}, \ldots, \bar{\mathcal{H}}_{(N-1)\phi}$. Since a phase shift of ϕ multiplies a m-quantum coherence by $e^{im\phi}$, to lowest order only 0, N, $2N$, ...-quantum coherences survive these shifts. Large enhancements for up to eight-quantum selections have been experimentally demonstrated (Ref. 23).

where m_i and m_j are the z axis quantum numbers of states i and j, respectively. Thus, a one-quantum coherence ($m_i - m_j = 1$) is shifted by $\exp(-i\phi)$, a two-quantum coherence is shifted by $\exp(-2i\phi)$, and so forth.

The shift is repeated to produce $\bar{\mathcal{H}}_{2\phi}$, $\bar{\mathcal{H}}_{3\phi}$, ... up to $\bar{\mathcal{H}}_{N\phi=2\pi}$. Now since the sequence is cyclic the propagator can be expanded in powers of $\Delta\tau_p$, with the lowest order term being

$$\bar{\mathcal{H}}^{(0)} = \sum_m \bar{\mathcal{H}}_{m\phi} . \tag{21}$$

Only operators with $m_i - m_j = 0, N, 2N, \ldots$ are unaffected by the phase shifts of $2\pi/N$. All other operators cancel. The only additional complication is to choose a sequence for $\bar{\mathcal{H}}_0$ which makes high-order correction terms negligible. Good four-quantum selection has been achieved with as few as four pulses for $\bar{\mathcal{H}}_0$.[24] Up to eight-quantum selection with strong signal enhancements have been observed with more complicated sequences.[23]

B. Optical selective excitation: vibrational overtones

The major experimental complication in studying multiphoton processes or highly excited vibrational states is that energy mismatches inhibit the pumping into these states. Figure 6 illustrates a typical situation for a simple three-level system, such as the ground state and first two overtones of some vibrational mode. The anharmonicity ω_Q is typically much larger than accessible values of $\boldsymbol{\mu} \cdot \boldsymbol{\epsilon}$. Thus, pumping at a frequency corresponding to half the energy difference between the ground and second excited states is similar, in a qualitative sense, to pumping two different two-level systems as in Fig. 1(b) (i.e., $\Delta\omega \gg \omega_1$). Roughly speaking, then, one might expect the multiple phase trains of Figs. 2 and 3 to overcome this offset in a similar manner. In particular, the fact that phase shifting creates sidebands in encouraging, because an appropriate choice of pulse lengths may make the sidebands coincide with the two allowed transitions.

This in fact turns out to be correct. The Hamiltonian for a three-level system interacting with an applied field can be generally written:

$$\mathcal{H} = \hbar[\omega_0\sigma_z + \omega_1 \cos(\omega t + \phi)\sigma_x + \omega_Q\sigma_z^2] , \tag{22}$$

where the angular momentum matrices are given by

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 2^{-1/2} & 0 \\ 2^{-1/2} & 0 & 2^{-1/2} \\ 0 & 2^{-1/2} & 0 \end{pmatrix},$$

$$\sigma_z^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i2^{-1/2} & 0 \\ i2^{-1/2} & 0 & -i2^{-1/2} \\ 0 & i2^{-1/2} & 0 \end{pmatrix} . \tag{23}$$

The matrices σ_x, σ_y, and σ_z are defined by analogy with a spin-1 nucleus[6]; there the ω_Q term comes from the quadrupolar interaction with electric field gradients. The assumptions so far are that only the transitions $|0\rangle \rightarrow |1\rangle$ and $|1\rangle \rightarrow |2\rangle$ have appreciable dipole moments, and that the two dipole moments are equal. Either of these assumptions may be relaxed, at the expense of including additional operators in $\mathcal{H}$.

In cases of physical interest the harmonic oscillator term $\omega_0\sigma_z$ is dominant. The rotating wave approximation then amounts to assuming that direct absorption at $2\omega_0$ can be neglected because that frequency is far from resonance for any allowed transition. For the values of ω_Q/ω_0 normally encountered in NMR at high fields ($\omega_Q \sim 10^5$ rad, $\omega_Q \sim 10^9$ rad) this assumption is quite good. It will also be valid for the slightly anharmonic vibrations discussed in the next section. This approximation gives

$$\mathcal{H} = \hbar(\Delta\omega\sigma_z + \omega_1 \cos\phi\sigma_x + \omega_1 \sin\phi\sigma_y + \omega_Q\sigma_z^2) . \tag{24}$$

The anharmonic oscillator $\omega_Q\sigma_z^2$ generates the only im

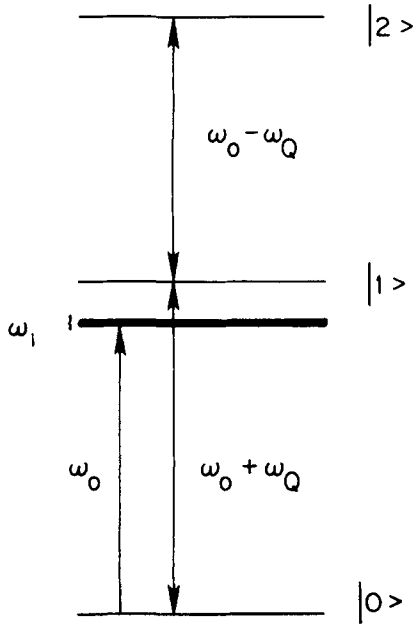

FIG. 6. Energy mismatches provide a fundamental limitation in multiphoton pumping. This figure illustrated a typical case with a ground state and two-excited states (for example, the fundamental and first overtone of a local vibrational mode). Generally only the $|0\rangle \rightarrow |1\rangle$ and $|1\rangle \rightarrow |2\rangle$ transitions are allowed, so the best way to pump population into $|2\rangle$ with a single frequency laser is to pump at half the $|0\rangle \rightarrow |2\rangle$ energy difference. But then the anharmonicity ω_Q puts $|1\rangle$ far off resonance, so pumping is inefficient.

portant difference between this system and the two-level systems of Sec. II. Since $\omega_Q \gg \omega_1$ in most physically interesting cases,[28] the $\omega_Q \sigma_z^2$ term is the one which must be used as $\mathcal{H}_{\text{blg}}$ in Eqs. (13) and (14). This is the opposite constraint from that used in NMR, where ω_1 dominates and the pulses generate the most important rotations.

Whenever $\omega_Q t = 2\pi$ we have

$$U = \exp(i2\pi\sigma_z^2) = \begin{pmatrix} e^{+2\pi i} & 0 & 0 \\ 0 & e^{0} & 0 \\ 0 & 0 & e^{+2\pi i} \end{pmatrix} = 1 . \tag{25}$$

Thus the net effect of $\omega_Q \sigma_z$ alone after a time $t = 2\pi/\omega_Q$ is zero. Equation (13) then shows that, for a time independent Hamiltonian $\mathcal{H}_{\text{int}}$,

$$\bar{\mathcal{H}}_{\text{int}}(t + 2\pi/\omega_Q) = \bar{\mathcal{H}}_{\text{int}}(t) .$$

If $\mathcal{H}_{\text{int}}$ is instead time dependent (i. e., a pulse sequence) then its effects will only build up if

$$\mathcal{H}_{\text{int}}(t + 2\pi/\omega_Q) = \mathcal{H}_{\text{int}}(t) .$$

In other words, the pulse sequence must repeat itself after $t = 2\pi/\omega_Q$.

Consider first a single long excitation pulse with $\Delta\omega = 0$ (the most favorable case) and no phase shifts. Then Eq. (13) gives

$$\bar{\mathcal{H}}_{\text{int}}(t) = \begin{pmatrix} 0 & \omega_1 e^{i\omega_Q t} & 0 \\ \omega_1 e^{-i\omega_Q t} & 0 & \omega_1 e^{-i\omega_Q t} \\ 0 & \omega_1 e^{i\omega_Q t} & 0 \end{pmatrix} \tag{26}$$

and Eqs. (15)–(17) give

$$\bar{\mathcal{H}}^{(0)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{27}$$

$$\bar{\mathcal{H}}^{(1)} = \begin{pmatrix} -\frac{1}{2}\omega_1^2/\omega_Q & 0 & -\frac{1}{2}\omega_1^2/\omega_Q \\ 0 & \omega_1^2/\omega_Q & 0 \\ -\frac{1}{2}\omega_1^2/\omega_Q & 0 & -\frac{1}{2}\omega_1^2/\omega_Q \end{pmatrix} . \tag{28}$$

To lowest order the pulse has no effect. Excited state population is pumped only through $\bar{\mathcal{H}}^{(1)}$, which is of order ω_1^2/ω_Q and therefore very small. Thus, excited state population is produced only very slowly.

Compare this to what happens if one phase shift is used at $t = \pi/\omega_Q$, making the pulse sequence $(x - \bar{x})$. Then

$$\bar{\mathcal{H}}_{\text{int}}(t) = \begin{pmatrix} 0 & 2^{-1/2}\omega_1 e^{i\omega_Q t} & 0 \\ 2^{-1/2}\omega_1 e^{-i\omega_Q t} & 0 & 2^{-1/2}\omega_1 e^{-i\omega_Q t} \\ 0 & 2^{-1/2}\omega_1 e^{i\omega_Q t} & 0 \end{pmatrix}, \quad 0 \le t < \pi/\omega_Q$$

$$= \begin{pmatrix} 0 & 2^{-1/2}\omega_1 e^{i\omega_Q T} & 0 \\ 2^{-1/2}\omega_1 e^{-i\omega_Q T} & 0 & 2^{-1/2}\omega_1 e^{-i\omega_Q T} \\ 0 & 2^{-1/2}\omega_1 e^{i\omega_Q T} & 0 \end{pmatrix}, \quad \pi/\omega_Q \le t \le 2\pi/\omega_Q , \quad T = (2\pi/\omega_Q) - t , \tag{29}$$

$$\bar{\mathcal{H}}^{(0)} = \begin{pmatrix} 0 & i\omega_1(2^{-1/2}2/\pi) & 0 \\ -i\omega_1(2^{-1/2}2/\pi & 0 & -i\omega_1(2^{-1/2}2/\pi) \\ 0 & i\omega_1(2^{-1/2}2/\pi) & 0 \end{pmatrix} \tag{30}$$

with $\bar{\mathcal{H}}^{(1)}$ the same as in Eq. (28). Since pulse effects survive in $\bar{\mathcal{H}}^{(0)}$ excited states will be far more efficiently pumped, by a factor of about ω_Q/ω_1 compared to the unshifted sequence. In fact, if $N = (\pi/4)(\omega_Q/\omega_1)$ then $\bar{\mathcal{H}}^{(0)}$ is a perfect π pulse, putting all the ground state population into the excited state. Note that this requires

$$t = [(\pi/4)(\omega_Q/\omega_1)](2\pi/\omega_Q) , \tag{31}$$

$$\omega_1 t = \pi^2/2 \tag{32}$$

so just as in the two-level case the pumping is achieved in short times. If the phase shift is replaced by a delay between pulses of $t_d = \pi/\omega_Q$ the zero-order Hamiltonian is reduced from Eq. (30) by about a factor of 2, since the pulse sequence now takes roughly twice as long. This is still a tremendous improvement over single pulse excitation, and as discussed in the last section this sequence can be created readily by an interferometer.

The sequence $(x - \bar{x})_N$ would be two-quantum selective in NMR, since it uses a 180° phase shift. However. the large optical enhancement we have just described is different from NMR two-quantum selection, since Eq. (30) shows that $\bar{\mathcal{H}}^{(0)}$ has no two-quantum operators present. The basic reason for the enhancement is illustrated in Fig. 7. The anharmonic oscillator term $\omega_Q \sigma_z^2$ is much larger than the laser interaction term, so any interaction which does not commute with σ_z^2 and is constant over one cycle of the anharmonic term $(2\pi/\omega_Q)$ will be averaged away to lowest order [Fig. 7(a)]; see also Eqs. (27) and (28). Phase shifts [Fig. 7(b)] or delays between pulses [Fig. 7(c)] break this averaging, allowing the laser to be much more effective.

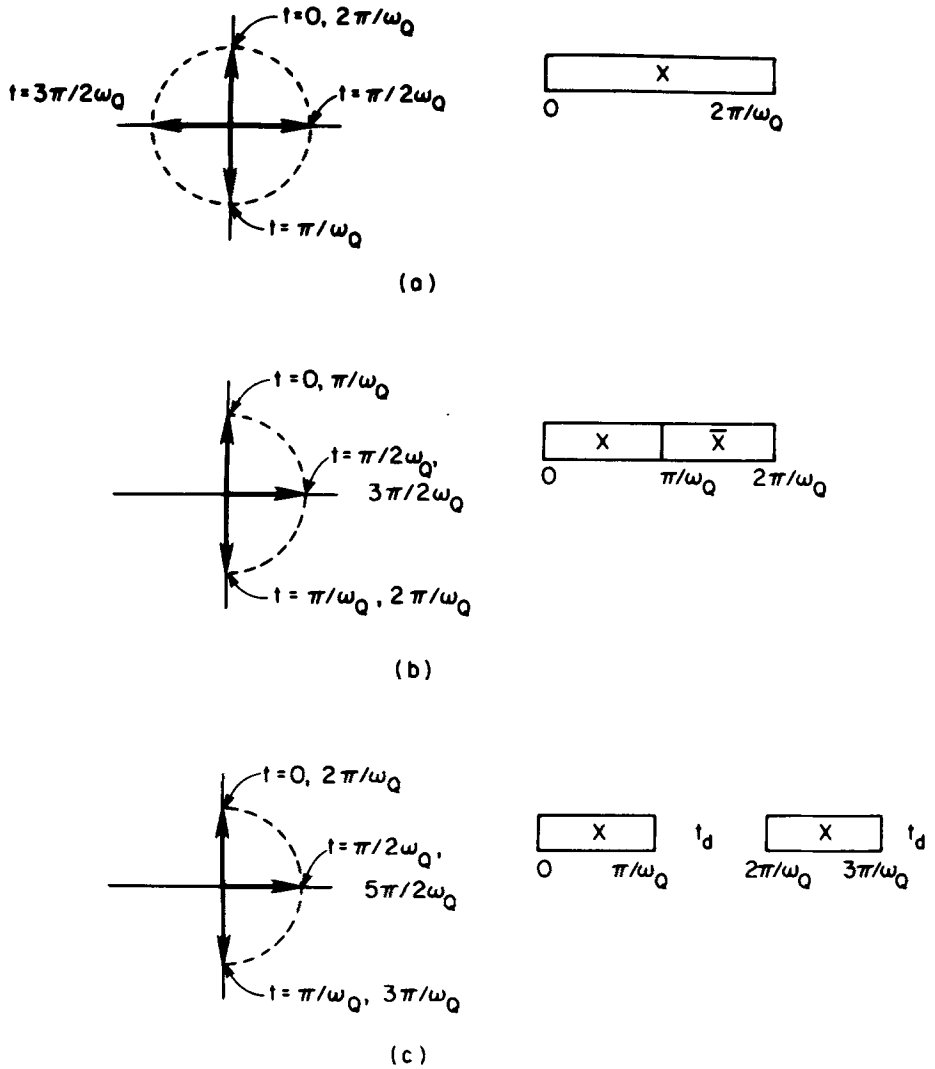

FIG. 7. Schematic illustration of the effects of rapid phase or amplitude modulation. In part (a) the anharmonicity ω_Q, which is much larger than the pulse bandwidth, averages away the laser interaction to lowest order over any interval of length $2\pi/\omega_Q$ [see Eq. (27)]. The modulation in part (b) or (c) destroys this averaging, thus dramatically increasing laser pumping efficiency [see Eq. (30)].

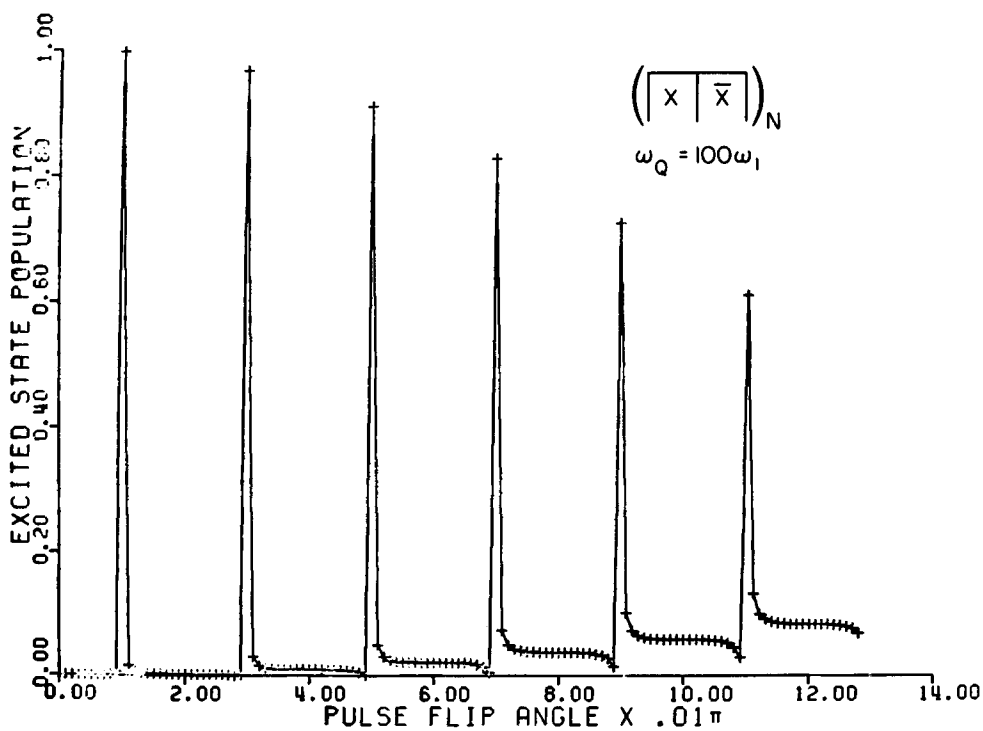

FIG. 8. A phase modulated sequence can overcome large anharmonicities when the pulse width is set to $t_p = (2n+1)\pi/(\omega_Q^2+\omega_1^2)^{1/2}$, where n is any integer. In that case the sequence is cyclic and coherent averaging is possible (see the text). In this specific example 78 repetitions, which would give a total on-resonance flip angle of 1.56 π, produce a complete population inversion for an anharmonicity 100 times larger than the pulse bandwidth (Rabi frequency). This sequence can be viewed qualitatively as in Fig. 2: values of pulse width which give π, 3π, 5π, ... rotations permit buildup of large inversions. A single long pulse could produce only 0.006 % excited state population in the time needed to produce complete inversion here.

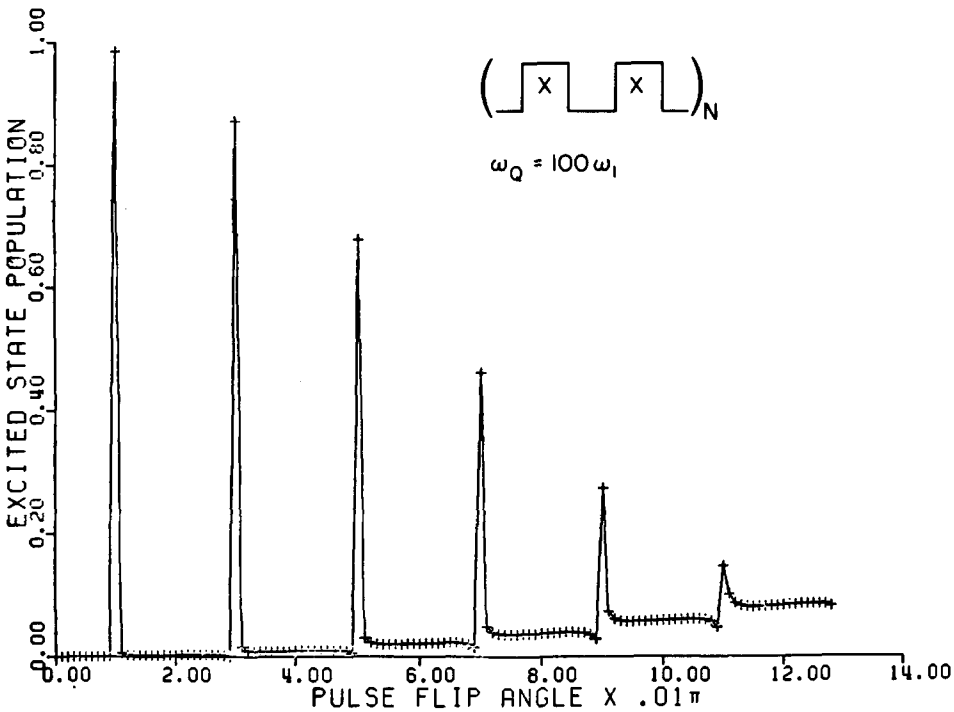

FIG. 9. Large anharmonicities can also be overcome by amplitude modulated sequences, which can be created by an interferometer. This sequence can be viewed qualitatively as in Fig. 3. We have equated the pulse and delay widths, which causes a small error in the cyclic condition for very long pulses (see the text). For short pulses the phase modulated and amplitude modulated sequences are equally efficient.

C. Calculations of the enhancement

The effects of the pulse trains $(X-\bar{X})_N$ and $(\frac{1}{2}t_d - X - t_d - X - \frac{1}{2}t_d)_N$ on three level systems with $\omega_Q = 100\ \omega_1$ were calculated for different pulse lengths on VAX 11/780 computers at Princeton University and the California Institute of Technology. Neither of these sequences has much effect except for pulse lengths t_p such that $(\omega_1^2+\omega_Q^2)^{1/2}t_p = (2N+1)\pi$ and delay lengths t_d such that $\omega_Q t_d = (2N+1)\pi$. At that point large effects are observed, reflecting the cyclic condition (see Figs. 8 and 9). When $\Delta\omega = 0$, which corresponds to irradiating at exactly half the $|0\rangle \rightarrow |2\rangle$ energy difference, 78 repetitions of $(X-\bar{X})$ put 99.6% of the population in the second excited state. This essentially complete inversion is expected, since $(\pi/4)(\omega_Q/\omega_1) = 78.4$ repetitions would be a perfect π pulse [Eq. (31)].

If the phase shifts are omitted, so that a single x pulse with the same total length as this sequence is applied, the second excited state population is only 0.006%. Comparison of Eqs. (28) and (30) show that the pulse flip angle should be only about $\omega_1/\omega_Q = 1\%$ as large, which agrees quite well with this result.

Excited state population is harder to pump when $\Delta\omega \neq 0$, because then another term $\Delta\omega\sigma_z$ is present in $\bar{\mathcal{H}}^{(0)}$ for all of these sequences. When $\Delta\omega = \omega_1$ a single X pulse with the same length as before pumps less than 0.003% into the second excited state. Selective sequences do not perform as well as they did when $\Delta\omega = 0$, but the increase is still substantial; a zero-order sequence with the same parameters as in Fig. 9 excites 0.6%, a gain of more than 200.

Further enhancements are possible with changes in the number of repetitions, or with additional phase shifts.[22] For example, 32 repetitions of the sequence $(X\bar{X}\bar{X}X)$ with $\Delta\omega = \omega_1$, and pulse width $t_p = \pi/2\omega_Q$ pumps 6.1% of the population into the second excited state.

IV. LOCAL VIBRATIONAL MODES

It is now known[29] that large molecules with CH bonds exhibit local CH-stretching vibrations especially in the high energy region ($\Delta v = 5, 6, \ldots$, etc., where v is the CH vibrational equation number). Modeling these local modes by a one-dimensional Morse oscillator, the energy of the local mode becomes

$$E(v) = \omega_e(v+\tfrac{1}{2}) - \chi(v+\tfrac{1}{2})^2 - D \tag{33}$$

$$= (\omega_e - \chi)v - \chi v^2 - D_0\ . \tag{34}$$

In the above expression, ω_e is the frequency and χ is the anharmonicity constant. D is the dissociation energy, and is related to D_0: $D = D_0 + \omega_e/2 - \chi/4$. The important point about the above relation is that $\Delta E(v)/v$ when plotted vs v gives a straight line with the slope giving χ. This turns out to be true for CH vibrations in a number of large molecules like benzene or naphthalene. Typical values for the parameters are

$$\omega_e \simeq 3100\ \text{cm}^{-1}\ ,\quad \chi \simeq 58\ \text{cm}^{-1}\ ,\quad D \simeq 41\,700\ \text{cm}^{-1}\ .$$

The energies of the first three levels can be rewritten by analogy with a spin-1 nucleus as

$$E(m) = (\omega_e - 3\chi)\sigma_z - \chi\sigma_z^2 - (D_0 + 2\chi)\ ,$$

where $m = v - 1$ is the z-axis quantum number of the analogous spin [see Eqs. (22) and (23)]. Picosecond or subpicosecond pulses of roughly 10^9 W peak power reflect the current state of the art.[30] For a tightly focused ($\sim 50\ \mu$) laser spot on a sample with a strongly allowed (~ 1 D) transition this gives $\omega_1 \sim 10^{11}$ rad, far short of $\chi = 10^{13}$ rad. Thus even if a laser with these specifications existed at $\omega_e - 3\chi = 2926\ \text{cm}^{-1}$ a 0.3 ps

pulse ($\omega_1 t_p = 0.03$) would be effectively scaled down by ω_1/χ, and would then give a second excited state population of less than 10^{-7}.

Now suppose this single pulse were split into 100 smaller pulses.[15] Each of these pulses would have ω_1 scaled down by about a factor of $\sqrt{100} = 10$. If they were separated by $t_d = 0.3$ ps ($\omega_Q t_d = \pi$) then the 1000:1 ratio between ω_Q and ω_1 would make 780 cycles a π pulse [see Eq. (31)]. Instead 50 cycles are available, giving a 0.2 rad pulse or an excited state population of about 1%—a gain of 10^5.

Larger excited state populations could be predicted by choosing other pulse sequence parameters. But all these calculations should be considered qualitative, since they ignore experimental complications such as relaxation effects and interferometer nonidealities. Nonetheless, multiple pulse trains are clearly capable of dramatically enhancing forbidden transitions, and applications to multiphoton pumping should be technically feasible in the near future.

V. CONCLUSIONS

The most significant limitation of coherent optical spectroscopy is the difficulty of producing powerful enough laser pulses to overcome inhomogeneous broadening or resonance frequency mismatches. We have shown that multiple pulse trains generated by phase modulation or amplitude modulation provide a technically feasible approach to dramatically increased population inversions and multiphoton pumping. We expect that this approach will improve the capabilities of currently available lasers in exciting different portions of highly inhomogeneously broadened transitions, and we anticipate that multiphoton pumping will also benfit from this approach.

ACKNOWLEDGMENTS

We wish to thank Luciano Mueller for useful discussion about NMR composite pulse sequences in three-level systems. W. S. W. held a National Science Foundation Postdoctoral Fellowship at Caltech during the initial stages of this work. This work was supported in part by the National Science Foundation under Grant No. DMR 81-05034 to the California Institute of Technology.

[1]W. S. Warren and A. H. Zewail, J. Chem. Phys. **75**, 5956 (1981).
[2]W. S. Warren and A. H. Zewail, J. Chem. Phys. (in press).
[3]For a review see A. H. Zewail, Acc. Chem. Res. **13**, 360
[4]R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, J. Appl. Phys. **28**, 49 (1957).
[5]T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR* (Academic, New York, 1971).
[6]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, London, 1963).
[7]T. G. Schmalz and W. H. Flygare, in *Laser and Coherence Spectroscopy*, edited by J. Steinfeld (Plenum, New York, 1978).
[8]R. L. Shoemaker, in Ref. 7. This is an excellent review for IR coherent transients.
[9]For a recent review see M. Burns, W. K. Liu, and A. Zewail, *Modern Problems in Solids State Physics* (North Holland, Amsterdam, 1982), Vol. 20.
[10]I. I. Rabi, N. F. Ramsey, and J. Schwinger, Rev. Mod. Phys. **25**, 157 (1964).
[11]R. Freeman, S. P. Kempsell, and M. H. Levitt, J. Magn. Reson. **38**, 453 (1980); M. H. Levitt and R. Freeman, *ibid.* **43**, 502 (1981); M. H. Levitt, R. Freeman, and T. Frenkel, *ibid.* **47**, 328 (1982).
[12]W. S. Warren and A. H. Zewail, J. Chem. Phys. (submitted).
[13]R. Alder, IEEE Spectrum **4**, 42 (1967); R. S. Bachrach, Rev. Sci. Instrum. **43**, 723 (1972); J. Sapriel, *Acousto-Optics* (Wiley–Interscience, New York, 1978).
[14]G. Morris and R. Freeman, J. Magn. Reson. **29**, 433 (1978).
[15]For the sake of mathematical simplicity we have oversimplified the actual effect of the interferometer. In reality the pulses out of the interferometer will grow smaller as energy couples out of the cavity. In addition, in cases of experimental interest the input pulse shape will not be square. Neither of these complications is serious. Increasing the finesse of the interferometer will allow more pulses to be coupled out before a significant power decrease occurs, at the expense of slightly decreased peak power. The only important effect of nonsquare pulses, as verified by our computer calculations, is to change the optimum pulse flip angles and delays slightly from the values discussed in the text.
[16]M. M. Salour, Opt. Commun. **22**, 202 (1977); M. M. Salour, *Coherence and Quantum Optics IV* (Plenum, New York, 1978), p. 367; M. M. Salour and C. Cohen-Tannodji, Phys. Rev. Lett. **38**, 757 (1977).
[17]M. E. Stoll, A. J. Vega, and R. W. Vaughan, J. Chem. Phys. **67**, 2029 (1977); A. Wokaun and R. R. Ernst, Mol. Phys. **36**, 317 (1978).
[18]S. Vega, T. W. Shattuck, and A. Pines, Phys. Rev. Lett. **37**, 43 (1976); G. Drobny, A. Pines, S. Sinton, D. P. Weitekamp, and D. Wemmer, Faraday Div. Chem. Soc. Symp. **13**, 49 (1979).
[19]G. Rodenhausen, R. L. Vold, and R. R. Vold, J. Magn. Reson. **37**, 93 (1980); A. Wokaun and R. R. Ernst, Chem. Phys. Lett. **52**, 407 (1977); H. Hatanaka, T. Terao, and T. Hashi, J. Phys. Soc. Jpn. **39**, 835 (1975).
[20]J. B. Murdoch, W. S. Warren, D. P. Weitekamp, and A. Pines, J. Magn. Reson. (submitted).
[21]W. S. Warren, S. Sinton, D. P. Weitekamp, and A. Pines, Phys. Rev. Lett. **43**, 1791 (1979).
[22]W. S. Warren, D. P. Weitekamp, and A. Pines, J. Chem. Phys. **73**, 2084 (1981).
[23]W. S. Warren and A. Pines, J. Chem. Phys. **74**, 2808 (1981).
[24]W. S. Warren and A. Pines, Chem. Phys. Lett. **88**, 441 (1982).
[25]W. Magnus, Commun. Pure Appl. Math. **7**, 649 (1954).
[26]R. M. Wilcos, J. Math. Phys. **8**, 962 (1967); P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966).
[27]U. Haeberlen, *Advances in Magnetic Resonance* (Academic, New York, 1976), Suppl. 1.
[28]If the laser intensity is large enough to overcome energy mismatches ($\omega_1 \gg \omega_Q$) then population inversions can be a achieved in simpler ways. See, for example, M. M. T. Loy, Phys. Rev. Lett. **41**, 473 (1978).
[29]See, for example, J. W. Perry and A. H. Zewail, Chem. Phys. Lett. **65**, 31 (1979).
[30]For a brief review see A. G. Doukas and R. R. Alfano, *Photonics Spectra*, August 1982, p. 54.